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(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

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(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): PETTIFER, Robert, Michael [GB/GB]; 8 Waverly Avenue, Whitley Bay, Tyne & Wear NE25 8AU (GB). REID, Victor, Stuart [GB/GB]; 5 St. Julien Gardens, Cochrane Park, Heaton, Newcastle upon Tyne NE7 7LL (GB). SHERRINGTON, Paul [GB/GB]; 3 Jesmond Place, Newcastle upon Tyne NE2 3DF (GB). SUMMERS, Shirley [GB/GB]; 122 Bede Close, Holystone, Tyne & Wear NE12 9SN (GB).

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(54) Title: DETERGENT COMPOSITIONS OR COMPONENTS

(57) Abstract: The present invention relates to detergent compositions or components comprising certain hydrophobically modified cellulosic materials, which provides protection of fabrics, whereof at least 80 % or even at least 90 % has a particle size of below 1000 microns or even below 850 or even 710 microns. Selection of material of this particle size results in improved dispersancy of the cellulosic material and imparts improved appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

DETERGENT COMPOSITIONS OR COMPONENTS

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TECHNICAL FIELD

The present invention relates to detergent compositions or components comprising certain hydrophobically modified cellulosic materials, which provides protection of fabrics, of a specific particle size and preferably particle size distribution.

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BACKGROUND OF THE INVENTION

It is generally known that fabrics and textiles tend to wear out over time, due to mechanical action during washing but also in use. For example, short fibers are dislodged from the fabric and may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Co-pending application PCT/US98/19139 describes the use of hydrophobically modified cellulosic polymers which are found to provide excellent integrity benefits to fabrics. Without wishing to be bound by theory, it is believed that these materials associate themselves with the fibers of the fabrics and textiles during the wash and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance.

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These materials are not readily water-soluble and the delivery to the wash and to the fabrics thus very much depends on the dispersion of the material in the wash water. The inventors have found that under certain conditions, these hydrophobically modified cellulosic polymers are not always dispersed satisfactory, resulting in reduced performance and moreover localised residues of the material on the fabrics. Furthermore, the inventors also found that under certain conditions other detergent ingredients can become entrapped in the cellulosic material, causing further residue problems, or even reduced performance of these other ingredients.

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The inventors have now found that when hydrophobically modified cellulosic material of a specific particle size is used, these problems can be reduced or even avoided. They

found that when the selected material, preferably having a particle size of below 1000 microns, or even below 710 microns or even below 500 microns improved dispersion of the material is obtained, and furthermore improved dispersion or dissolution of other detergent ingredients being in close contact with the polymers. They also found that
5 hereby an improved efficiency of the hydrophobically modified cellulose material is obtained and thus an improved fabric integrity. They also found that it may hereby be preferred that the material has a narrow particle size distribution.

Co-pending application US 60/113306 describes that these hydrophobically modified
10 materials materials may be formed into agglomerates, for example with builders such as zeolite, and then incorporated into detergent compositions. The inventors have now found that when hydrophobically modified cellulose polymers of selected particle size are incorporated in these pre-formed particles, such as agglomerates but also spray dried blown powders, also improved dispersion or dissolution of the preformed particles, and
15 also the ingredient and importantly the cellulose material therein is achieved.

SUMMARY OF THE INVENTION

20 The present invention relates to a detergent composition or component comprising a hydrophobically modified cellulosic material, whereof at least 80% or even at least 90% or even 100% has a particle size of below 1000 microns, preferably below 850 microns or even below 710 microns.

25 The hydrophobically modified cellulosic material may be incorporated in the compositions or components as dry-add, and/ or the hydrophobically modified cellulosic material may be present in a pre-formed particle such as an agglomerate, spray dried or blown powder or extrudate, together with other detergent ingredients.

30 The compositions may be laundry detergents or additives, fabric softeners or fabric treatment products. Preferably the compositions or components are solid, preferably

granular or in the form of a tablet, however liquid, non-aqueous liquid and gel compositions are also envisaged herein.

5 The present invention also relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions or components described herein.

DETAILED DESCRIPTION OF THE INVENTION

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Hydrophobically Modified Cellulosic Material and Polymers

The hydrophobically modified cellulosic material, herein also referred to as cellulosic material, are such that at least 80% or even 90% by weight but preferably 100% by weight has a particle size of below 1000 microns. However, it may be preferred that at least 80%
15 by weight or even 90% or even 100% by weight has a particle size of below 850 microns or even below 710 microns or even below 500 microns.

To obtain the benefits of the invention, the exact particle size and the particle size distribution or span of the hydrophobically modified cellulosic material may vary within
20 the specified range, depending on the mode the material is incorporated in the compositions or components and also on the exact nature of the compositions and components.

When the cellulosic material is added as a dry-add, as described herein, it may be
25 preferred that the material has a particle size of between 1 micron to 1000 microns, more preferably 80% having a particle size of from 10 microns to 900 microns, more preferably 80% having a particle size of from 50 or even from 150 or even from 250 microns to 850 or even to 800 or even to 710 microns. The mean particle size of the celulosic material is then preferably from 100 to 850 microns, more preferably from 250 microns to 800
30 microns or even from 350 microns to 800 microns.

When the cellulosic material is incorporated in a preformed particle, as described herein, it may be preferred that the material has a particle size of between 0.1 micron to 710 microns, more preferably 80% having a particle size of from 1 micron to 550 microns, more preferably 80% having a particle size of from 2 or even from 10 or even from 25
5 microns to 500 or even to 450 or even to 350 microns. The mean particle size of the celulosic material is then preferably from 5 to 500 microns, more preferably from 25 microns to 450 microns or even from 50 microns to 400 microns.

— In certain applications, it may be beneficial that the particle size distribution is narrow, for
10 example having a span of 3 or less, preferably 2 or less, even more preferably 1.7 or even 1.5 or less.

As used herein, the phrase "mean particle size" means the geometric mass median diameter of a set of discrete particles as measured by any standard mass-based particle
15 size measurement technique, preferably by dry sieving. As used herein, the "span" of a particle size distribution means the geometric standard deviation, which for example can be calculated by the geometric breadth of the best-fitted log-normal function to the above-mentioned particle size data which can be accomplished by the ratio of the diameter of the 84.13 percentile divided by the diameter of the 50th percentile of the cumulative
20 distribution ($D_{84.13}/D_{50}$); See Gotoh et al, *Powder Technology Handbook*, pp. 6-11, Marcel Dekker 1997.

The cellulosic material of the specified particle size can be obtained by any method of selecting material based on particle size. Preferred may be that larger granules of the
25 material are reduced in particle size by grinding or milling, followed by sieving the obtained smaller particles and selecting the required sieve fractions. Other methods are known to the skilled person. It may be preferred that one fraction is used as dry-add for the compositions or components herein, and that another fraction is incorporated in preformed particles, as described hereinafter.

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Typically, the hydrophobically modified cellulosic material comprises from 40% to 100% of hydrophobically modified polymers described herein after, more preferably from 50%

to 99% or even from 60% or even from 70% to 90% by weight of the material. The remaining weight % typically comprises impurities introduced during the making process, such as water, salts, and minor organic compounds which may include alcohols, organic acids or salts thereof, and/ or process aids.

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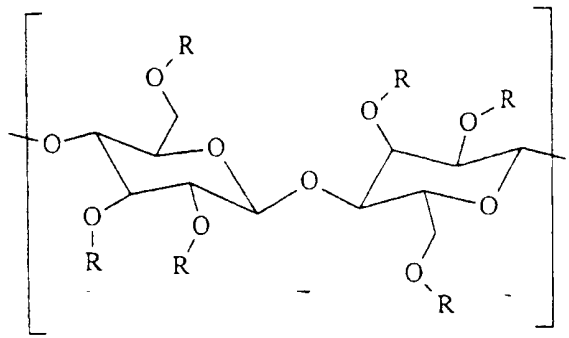
Depending on the application of the composition or component herein, the amount of cellulosic material in the compositions or components may vary. The cellulosic material will generally be about 0.01% to about 90% by the weight of the detergent composition or component, more preferably from 0.05% to 20% or even from 0.05% to 15% by weight.

10 In detergent compositions herein it may for example be preferred that the cellulosic material is present at a level of from 0.05% to 10% by weight of the detergent composition, preferably from 0.05% to 5% or even from 0.05% to 3% or even 0.1% to 2% by weight. In detergent additives or components, or the preformed particles described herein after, the material may preferably be present at a level of 0.05% to 40% by weight
15 of the component, or even from 0.05% to 20% or even 0.1% to 15% or even 1% to 10% by weight.

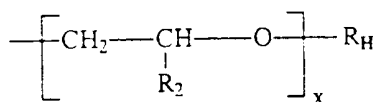
The cellulosic material herein is preferably present in the composition or component in such an amount that the concentration of the hydrophobically modified cellulosic polymer
20 in the wash is from 1 ppm to 10,000 ppm, preferably from 10 ppm to 7000 ppm or even from 20 to about 1000 ppm.

The hydrophobically modified cellulosic polymers in the material herein include polymers, oligomers, copolymers and also cross-linked polymers, oligomers and
25 copolymers. As will be apparent to those skilled in the art, an oligomer is a molecule consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. One suitable type of cellulosic
30 polymer herein has an average molecular weight of from about 5,000 to about 2,000,000, preferably from about 50,000 to about 1,000,000.

The cellulosic polymer for use herein is preferably of the following formula:



wherein each R is selected from the group consisting of R_2 , R_C , and



wherein:

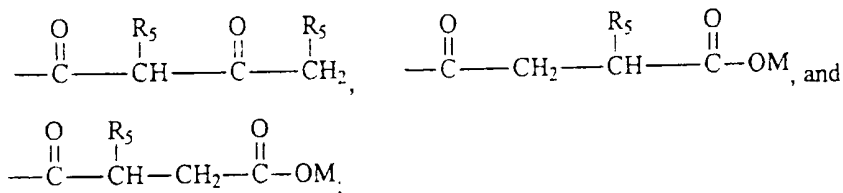
- each R_2 is independently selected from the group consisting of H and C_1 - C_4 alkyl;

- each R_C is $\text{---}(\text{CH}_2)_y\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}\text{OZ}$,

wherein each Z is independently selected from the group consisting of M, R_2 , R_C , and

R_H ;

- each R_H is independently selected from the group consisting of C_5 - C_{20} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{20} alkylaryl, C_7 - C_{20} arylalkyl, substituted alkyl, hydroxyalkyl, C_1 - C_{20} alkoxy-2-hydroxyalkyl, C_7 - C_{20} alkylaryloxy-2-hydroxyalkyl, $(R_4)_2$ N-alkyl, $(R_4)_2$ N-2-hydroxyalkyl, $(R_4)_3$ N-alkyl, $(R_4)_3$ N-2-hydroxyalkyl, C_6 - C_{12} aryloxy-2-hydroxyalkyl,



- each R_4 is independently selected from the group consisting of H, C_1 - C_{20} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{20} alkylaryl, C_7 - C_{20} arylalkyl, aminoalkyl, alkylaminoalkyl,

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dialkylaminoalkyl, piperidinoalkyl, morpholinoalkyl, cycloalkylaminoalkyl and hydroxyalkyl;

- each R_5 is independently selected from the group consisting of H, C_1 - C_{20} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{20} alkylaryl, C_7 - C_{20} arylalkyl, substituted alkyl, hydroxyalkyl, $(R_4)_2N$ -alkyl, and $(R_4)_3N$ -alkyl;

wherein:

M is a suitable cation preferably selected from the group consisting of Na, K, $1/2Ca$, and $1/2Mg$;

each x is from 0 to about 5;

each y is from about 1 to about 5; and

provided that:

- the Degree of Substitution for group R_H is between about 0.001 and 0.1, more preferably between about 0.005 and 0.05, and most preferably between about 0.01 and 0.05;
- the Degree of Substitution for group R_C wherein Z is H or M is between about 0.2 and 2.0, more preferably between about 0.3 and 1.0, and most preferably between about 0.4 and 0.7;
- if any R_H bears a positive charge, it is balanced by a suitable anion; and
- two R_4 's on the same nitrogen can together form a ring structure selected from the group consisting of piperidine and morpholine.

The "Degree of Substitution" for group R_H , which is sometimes abbreviated herein " DS_{RH} ", means the number of moles of group R_H components that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above.

The "Degree of Substitution" for group R_C , which is sometimes abbreviated herein " DS_{RC} ", means the number of moles of group R_C components, wherein Z is H or M, that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above. The requirement that Z be H or M is necessary to insure that there are a sufficient number of carboxy methyl groups such that the resulting polymer is soluble. It is understood that in

addition to the required number of R_C components wherein Z is H or M, there can be, and most preferably are, additional R_C components wherein Z is a group other than H or M.

These polymers can for example be obtained by use of processes as described in co-
5 pending application PCT/US98/19139 and PCT/US98/19142.

Highly preferred modified cellulosic polymers herein have the following specific
parameters, varying per polymer, and the following general parameters, applicable to each
- of these highly preferred polymers.

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General Polymer Parameters

Molecular Parameters	Description
Polymer Backbone	Carboxymethylcellulose
Degree of Carboxymethylation	$DS_{RC} = 0.3 - 2.0$; preferred $DS_{RC} = 0.5 - 0.70$.
Distribution of Carboxymethyls	Even and random distribution of carboxymethyls along the backbone
Molecular Weight	Mw: 5,000 - 2,000,000. Preferred: medium (approx 250,000 g/mol)
Type of Modification	Ether modification (in addition to carboxymethylation). Mixed cellulose ether
Level of Modification	$DS_{RH} =$ about 0.001 to about 0.1

Specific Polymer Parameters

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ID	Polymer	Type of Modification***	Preferred method of making
*A	Hexyl CMC	Hexyl ether	Chlorohexane added to CMC making process
*B	Decyl CMC	Decyl ether	Chlorodecane added to CMC making process
**C	C12-C13 alkoxy-2-hydroxypropyl CMC	C12-C13 alkoxy-2-hydroxypropyl ether	C12-C13 alkyl glycidyl ether added to CMC making process
*D	Hexadecyl CMC	Hexadecyl ether	Chlorohexadecane added to CMC making process
*E	Chloride salt of 3-trimethylammonio-2-hydroxypropyl ether of CMC	chloride salt of 3-trimethylammonio-2-hydroxypropyl ether	2,3-epoxypropyltrimethyl ammonium chloride added to the CMC making process
*F	$[-(C(O)-CH(C_{16}H_{33})-C(O)CH_2(C_{16}H_{33}))]$ ester of CMC or 1,3-dioxo-2-hexadecyloctadecyl ester of CMC		Cetyl Ketene Dimer added to CMC making process.

CMC = Carboxymethylcellulose

* Manufactured by Metsa Specialty Chemicals

** Manufactured by Akzo

*** DS_{RH} for these materials was in the range of from about 0.001 to about 0.1

Detergent Compositions and Components

The hydrophobically modified cellulosic material may be included in the detergent composition or components herein in the form of separate particles of the particle size specified herein, so-called dry-adds, which consisting essentially of the polymeric material.

The hydrophobically modified cellulosic material may also be present in a premix with other detergent active ingredients, and/ or in the form of preformed particles comprising the material and other detergent active ingredients.

The premix herein may be any pre-mix formed by mixing the cellulosic material and one or more other detergent ingredients together.

Suitable pre-formed particles herein, can be formed mixing the cellulosic material with other ingredients, and then by spray-drying, agglomeration, marumerisation, extrusion or compaction of the mixture, all of which methods for combining detergent ingredients are well-known in the art. Particularly preferred preformed particles are powders obtained from spray-drying processes, agglomerates and extrudates. Suitable spray-drying processes for forming such preformed particles are described for example in EP-A-763594 or EP-A-437888. Suitable processes for forming preformed particles which are agglomerates are described for example in co-pending application US 60/113306, but also in WO93/25378, EP-A-367339, EP-A-420317 or EP-A-506184 and suitable processes for forming preformed particles by extrusion are described for example in WO91/02047.

The preformed particle or premixes preferably comprise a carrier material and/ or a binding material, preferably including a surfactant.

This binding material can be any ingredient capable of binding or sticking the ingredients together. Highly preferred binding materials are surfactants, in particular anionic and nonionic surfactants. Most preferably at least an anionic surfactant is present. Suitable surfactants are described herein after. Other binding materials include polyethylene

glycols, polyvinyl acetyl amines, polyacrylates an/ or maleates, polyvinyl pyrrolidones and derivatives thereof, or mixtures thereto.

The carrier material can be any particulate ingredient. Useful particulate materials including inorganic or organic acids or salts and builder materials such a silicates. In particular useful carrier materials include sulphate salts, phosphate salts, carbonate salts, bicarbonate salts, inorganic peroxygen salts, organic carboxylic acids and salts thereof, amorphous silicates, crystalline (layered) silicates, aluminosilicates and mixtures thereof. Preferably at least an aluminosilicate is present.

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Other detergent ingredients

The compositions or components in accord with the invention also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

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They preferably contain at least a surfactant and a builder, preferably also one or more additional detergent ingredients selected from additional surfactants and builders, bleaches, bleach catalysts, alkalinity systems, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents soil releasing agents, perfumes, brightners, photobleaching agents, fabric softening agents, such as clays and cationic softeners, additional fabric care agents, and additional corrosion inhibitors.

20

Preferred additional ingredients are cyclic amine based polymers as described in co-pending application PCT/US98/19143 and PCT/US98/19141, which can provide additional fabric integrity benefits, in particular those compounds described therein in the examples, in particular example 1 and 2. These polymers may be present at a level of from 0.01% to 10% by weight of the composition or component, more preferably at a level of from 0.05% to 5% by weight or even form 0.1% to 2% by weight of the composition, or at a level of from 0.05% to 30% by weight of the component, more

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preferably at a level of from 0.1% to 20% by weight or even from 0.3% to 10% by weight of the component.

5 It may be preferred that when the hydrophobically modified polymeric material is present in an preformed particle, that the cyclic amine based polymers or part thereof, are present in the same preformed particle.

Surfactant

10 The components or compositions in accord with the invention preferably contain one or more surfactants selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

Anionic Surfactant

15 The components or compositions in accord with the present invention preferably comprise at least an anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent components or compositions.

20 These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate, including alkyl ethoxy carboxylates and soaps, and sarcosinate surfactants. Anionic sulfate and sulfonate surfactants are preferred.

Also preferred are dianionic surfactants containing, preferably two sulphate or sulphontae groups or a sulphate and sulphonate group.

25 Highly preferred are surfactants systems comprising a sulfonate and a sulfate surfactant, preferably a linear or branched alkyl benzene sulfonate and alkyl sulphates and/ or alkyl ethoxysulfates, as described herein.

30 Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts

of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Certain soaps may also be included as suds suppressers.

- 5 Other anionic surfactants include N-acyl sarcosinates, isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters). Resin acids and hydrogenated resin acids are also suitable, such as rosin,
- 10 hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic Sulfate Surfactant

- 15 Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

- 20 Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

- 25 Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and/ or sulfonate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

5 Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures
10 thereof.

Alkoxylated Nonionic Surfactant

15 Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic
20 ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic Alkoxylated Alcohol Surfactant

25 The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20
30 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 - C_{19} alkyl or alkenyl, more preferably straight-chain C_9 - C_{17} alkyl or alkenyl, most preferably straight-chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl.

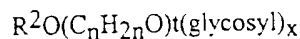
Nonionic Fatty Acid Amide Surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula:



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Cationic surfactants

It may be preferred to include cationic surfactants in the compositions or components herein. Preferred are quaternary ammonium surfactants.

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The levels of the quaternary ammonium surfactants used in detergent compositions of the invention are preferably from 0.1% to 20%, preferably from 0.4% to 7%, most preferably from 0.5% to about 5.0%, by weight of the detergent composition. The levels of the quaternary ammonium surfactants in components or additives of the invention are

10 preferably from 0.1% to 90%, preferably from 0.5% to 50%, most preferably from 2% to about 30%, by weight of the detergent component or additive.

Preferably, the cationic surfactant herein is selected from the group consisting of cationic mono-alkoxylated amine surfactants, cationic bis-alkoxylated amine surfactants and

15 mixtures thereof. Preferred are salts of the cationic C₁₂ - C₁₄ alkyl dimethyl ammonium ethanol surfactant.

20

Softener compounds

Preferably, the compositions or components herein comprise one or more softening compound. Preferred are clays, such as bentonite clay.

25 Also useful are quaternary ammonium softening compounds having one or two C₁₂-C₂₄ alkyl or alkenyl chains, optionally substituted with one or more functional groups such as -OH, -O-, CONH, -COO-, and with two or three C₁-C₁₁, preferably C-C₆ or even C₁ to C₄ alkyl or alkenyl groups, optionally substituted with a functional groups such as -OH, -O-, CONH, -COO- or mixtures thereof. Preferably, they are di-long-chain amides as

30 disclosed in EP-B-0 242 919. Preferably, when comprising two C₁₂-C₂₄ groups, they comprise two C₁-C₄ groups, preferably methyl or ethyl groups. When the softeners comprise three C₁-C₁₁ alkyl or alkenyl groups, they preferably comprise an C₁₈-C₂₄

alkyl or akenyl group. The anion is preferably chloride or bromide. Other preferred cationic softeners are for example described in US 5,540,850.

Perhydrate Bleaches

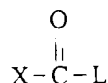
- 5 An preferred additional components of the components or compositions is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid.
- 10 Potassium peroxymonopersulfate, sodium per is another optional inorganic perhydrate salt of use in the detergent components or compositions herein.

Organic Peroxyacid Bleaching System

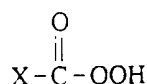
- A preferred feature of the components or compositions is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound or a preformed peroxyacid or mixtures thereof. When a preformed peroxyacid is present, it may be preferred to use only reduced levels of hydrogen peroxide sources or even omit any hydrogen peroxide source. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the components or compositions. Components or compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.
- 15
- 20
- 25

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as

-18-



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



5

Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

10

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

15

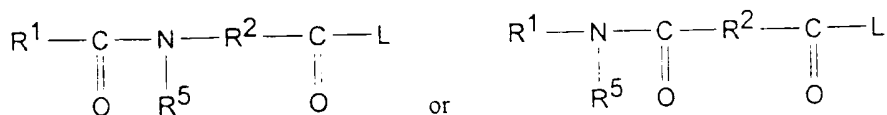
Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N',N' tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

20

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

25

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:

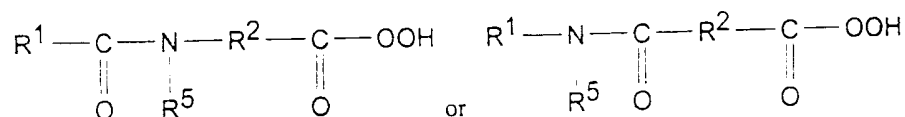


wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The detergent composition may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:

15



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Water-Soluble Builder Compound

The components or compositions in accord with the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 60% by weight, most preferably from 15% to 40% by weight of the composition.

The detergent components or compositions of the invention preferably comprise phosphate-containing builder material. Preferably present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40.

10

The phosphate-containing builder material preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous sodium tripolyphosphate.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of any of the foregoing. The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

20

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

30

The most preferred polycarboxylic acid containing three carboxy groups is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight of the composition.

- 5 Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed
- 10 citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

- Suitable examples of water-soluble phosphate builders are the alkali metal
- 15 tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

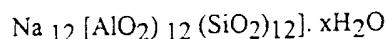
20 Partially Soluble or Insoluble Builder Compound

The components or compositions in accord with the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 0.5% to 60% by weight, preferably from 5% to 50% by weight, most preferably from 8% to 40% weight of the composition.

- 25 Examples of largely water insoluble builders include the sodium aluminosilicates.

- Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5,
- 30 preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS
5 and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula Na_{86}
10 $[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Another preferred aluminosilicate zeolite is zeolite MAP builder.

The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

15

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

20

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size,
25 expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional
30 analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Other preferred builder material includes crystalline layered silicates, such as sodium SKS-6, available from Clariant.

5 Heavy metal ion sequestrant

The components or compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show
10 selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 10%, preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably from 0.3% to 2% by weight of the compositions or component

15

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

20 Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

25 Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

30 Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic

acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

5

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-
10 N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali
15 metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Enzyme

Another preferred ingredient useful in the components or compositions herein is one or
20 more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent
25 components or compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S
30 (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into

the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/US 9703635, and in WO95/26397 and WO96/23873.

10

Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Hoge-Jensen et al, issued March 7, 1989.

30

Additional organic Polymeric Compound

In addition to the hydrophobically modified cellulosic material herein, additional organic polymeric compounds are preferred, preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent components or compositionss, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other preferred additional organic polymeric compounds suitable for incorporation in the detergent components or compositionss herein include additional non-hydrophobically modified cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

5

Highly preferred polymeric components herein are cotton and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517.

10 Suds Suppressing System

The detergent compositions of the invention, when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05% to 3% by weight of the composition.

15

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

20 Polymeric Dye Transfer Inhibiting Agents

The compositions herein may preferably also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents, preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these

25

Optical Brightener

The compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

30

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the components or compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

- 5 Highly preferred compositions contain from about 2% to about 10% by weight of an organic acid, preferably citric acid. Also, preferably combined with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent
10 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

Form of the Components or compositionss

- The components or compositions herein can take a variety of physical forms including
15 liquid and solid forms such as tablet, flake, pastille and bar, and preferably granular forms. The components or compositions can be made via a variety of methods, depending on their product form. The solid compositions or components can be made by methods such as dry-mixing, agglomerating, compaction, or spray-drying of the various compounds comprised in the detergent component, or mixtures of these techniques.

- 20 Detergent compositions and components herein preferably have a bulk density of from 300g/litre or even 350g/litre or 450g/litre to preferably 1500g/litre or 1000g/litre or even to 850g/litre.

25 Fabric Laundering Method

- The present invention also provides a method for laundering. Such a method employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent components or compositions herein before described or formed from the individual components of such components or compositions. Contacting of
30 fabrics with washing solution will generally occur under conditions of agitation although the components or compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment. As discussed

above, it is preferred that the washing solution have a pH of less than about 11.0, preferably it has a pH of less than 10.5 and most preferably it has a pH of less than 9.5.

5 An effective amount of a high density liquid or granular detergent components or compositions in the aqueous wash solution in the washing machine is preferably from about 500 to about 10000 ppm or even 7000 ppm, more preferably from about 1000 to about 3000 ppm.

10 The detergent components or compositions herein may also be used to treat and condition fabrics and textiles. Thus, for example, a fabric conditioning components or compositions comprising the hydrophobically modified cellulosic materials as described herein, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described. Then, 15 preferably at least about 1%, preferably from about 10%, more preferably from about 20% to about 80%, more preferably to about 60% by weight, of the composition or component is one or more fabric softener actives, such as cationically charged hydrocarbons, such as C12-C22 dialkyl substituted quaternary ammonium salts and/ or clays, optionally with a flocculating polymer.

20 Alternatively, the composition or component herein may be present in or in the form of a softening and cleaning composition, such as for example described in EP-B1-313146 and WO93/ 01267, preferably comprising additional softening ingredients, such as clay and optionally a flocculating polymer.

25

Abbreviations used in the detergent composition examples

30 LAS : Sodium linear C11-13 alkyl benzene sulfonate
TAS : Sodium tallow alkyl sulfate

	CxyAS	:	Sodium C1x - C1y alkyl sulfate
	CxyEzS	:	Sodium C1x-C1y alkyl sulfate condensed with z moles of ethylene oxide
5	CxyEz	:	C1x-C1y predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
	QAS	:	R2.N+(CH3)2(C2H4OH) with R2 = C12 - C14 alkyl
	QASA	:	R2.R3.N+(CH3)2 with R2 and R3 independently being C12 - C24 alkyl
10	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
	STS	:	Sodium toluene sulphonate
	CFAA	:	C12-C14 (coco) alkyl N-methyl glucamide
	TFAA	:	C16-C18 alkyl N-methyl glucamide
	TPKFA	:	C12-C14 topped whole cut fatty acids
15	STPP	:	Anhydrous sodium tripolyphosphate
	TSPP	:	Tetrasodium pyrophosphate
	Zeolite A	:	Hydrated sodium aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
20	NaSKS-6	:	Crystalline layered silicate of formula d- $\text{Na}_2\text{Si}_2\text{O}_5$
	Malic acid	:	Anhydrous malic acid
	Maleic acid	:	Anhydrous maleic acid
	Tartaric acid	:	Anhydrous tartaric acid
25	Carbonate	:	Anhydrous sodium carbonate
	Bicarbonate	:	Anhydrous sodium bicarbonate
	Silicate	:	Amorphous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$)
	Sulfate	:	Anhydrous sodium sulfate
	Mg sulfate	:	Anhydrous magnesium sulfate
30	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm

	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
	MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
5	AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
	CABP	:	Cyclic amine based polymer as described in PCT/US98/19143 and PCT/US98/19141 in examples 1 and 2 in table
10	HMC I	:	Hydrophobically modified cellulosic material comprising one or more of the polymers numbered A to F, described in the tables on p.6-7, whereof 80% by weight has a particle size of from 10 to 450 microns
15	HMC II	:	Hydrophobically modified cellulosic material comprising one or more of the polymers numbered A to F, described in the tables on p.6-7, whereof 80% by weight has a particle size of from 350 to 850 microns
	AC	:	Hydrophobically modified amide cellulose having an amide group comprising 2 to 12 carbon atoms
	CMC	:	Sodium carboxymethyl cellulose
20	Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
	PB4	:	Particle containing sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O}$
	PB1	:	Particle containing anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
25	Percarbonate	:	Particle containing sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	:	Particle comprising nonanoyloxybenzene sulfonate in the form of the sodium salt, the particles having a weight average particle size of 750 microns to 900 microns
30	NAC-OBS	:	Particle comprising (6-nonamidocaproyl) oxybenzene sulfonate, the particles having a weight average particle size of from 825 microns to 875 microns

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	TAED	:	Tetraacetylenediamine
	DTPA	:	Diethylene triamine pentaacetic acid
	DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
5	Brightener	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl or disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2,2'-disulfonate
	EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
10	HEDP	:	1,1-hydroxyethane diphosphonic acid
	PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
	PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000
	PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
15	PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
	PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
20	QEA	:	bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30
	SRP	:	Anionically end capped poly esters
	PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per
25		:	nitrogen
	Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1

30 In the following examples all levels are quoted as % by weight of the composition:

Examples of preformed particles G to J comprising any of the HMC I:

Particle	G	H	I	J
HMC I	14.0	3.0	5.0	10.0
CABP	6.0	-	-	-
Zeolite	-	33.0	25	30.0
Water	10.0	-	6.0	10.0
LAS or AS	40.0	20.0	-	20.0
AE3, AE5 or AE7	-	-	-	-
PVNO or PVP	-	-	34	-
AA or MA/AA	27.0	20.0	-	-
Brightener	-	-	-	5.0
Sodium Carbonate	-	24.0	25.0	15.0
CMC/PEG	3.0	-	5.0	-
total	100.0	100.0	100.0	100.0

5

TABLE III

The following compositions are in accordance with the invention.

	N	O	P	Q	R	S	T	U	V
<u>Spray-dried Granules</u>									
LAS	10.0	10.0	15.0	5.0	5.0	10.0	-	-	-
MBAS	-	-	-	5.0	5.0	-	-	-	-
C ₄₅ AS	-	-	1.0	-	2.0	2.0	-	-	-
C ₄₅ AE ₃ S	-	-	-	1.0	-	-	-	-	-
QAS	1.0	1.5	1.0	1.0	0.5	0.8	-	-	-
HMC I	0.3	0.8	1.5	1.0	0.9	1.3	-	-	-
MgSO ₄	0.5	0.5	0.1	-	-	-	-	-	-
Sodium citrate	-	-	-	3.0	5.0	-	-	-	-
Sodium carbonate	10.0	7.0	15.0	-	-	10.0	-	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-	-
Sodium silicate 1.6R	-	-	-	-	2.0	-	-	-	-
Zeolite A	16.0	18.0	20.0	20.0	-	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-	-
MA/AA or AA	1.0	2.0	11.0	-	-	2.0	-	-	-

PEG 4000	-	2.0	-	1.0	-	1.0	-	-	-
QEA	1.0	-	-	-	1.0	-	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-	-
<u>Agglomerate</u>									
LAS	-	-	-	-	-	-	2.0	2.0	-
MBAS	-	-	-	-	-	-	-	-	1.0
C ₄₅ AS	-	-	-	-	-	-	2.0	-	-
AE ₃	-	-	-	-	-	-	-	1.0	0.5
Carbonate	-	-	-	-	-	-	1.0	1.0	-
Sodium citrate	-	-	-	-	-	-	-	-	5.0
CFAA	-	-	-	-	-	-	-	-	-
Citric acid	-	-	-	-	-	-	-	1.0	1.0
QEA	-	-	-	-	-	-	2.0	-	-
SRP	-	-	-	-	-	-	1.0	0.2	-
Zeolite A	-	-	-	-	-	-	26.0	15.0	16.0
Sodium silicate	-	-	-	-	-	-	-	-	-
PEG	-	-	-	-	-	-	4.0	-	-
HMC I	-	-	-	-	-	-	5.0	-	-
<u>Builder Agglomerates</u>									
SKS-6	-	-	-	-	-	3.0	-	7.0	10.0
LAS	-	-	-	-	-	3.0	-	10.0	12.0
<u>Dry-add particulate components</u>									
Any of Particle G to J	-	-	-	-	10.0	5.0	-	2.0	4.0
NACAOBS	3.0	-	-	4.5	-	-	-	2.5	-
NOBS	1.0	3.0	3.0	-	-	-	-	-	5.0
TAED	2.5	-	-	1.5	2.5	6.5	-	1.5	-
Citrate/ citric acid	-	-	-	4.0	-	5.0	-	-	5.0

Percarbonate	15.0	3.0	6.0	10.0	-	-	24.0	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.3	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate	0.0	10.0	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsulated)	-	0.5	0.5	-	0.3	-	0.2	-	-
Suds suppressor	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
HMC II	1.0	0.5	-	-	-	-	-	-	-
Dyed carbonate (blue, green)	0.5	0.5	1.0	2.0	-	0.5	0.5	0.5	1.0
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1	-	0.6	0.3
Dye	-	-	-	0.3	0.05	0.1	-	-	-
AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	1.0	0.5	1.1	0.8	0.3	0.5	0.3	0.5	-
Fillers up to 100%									

TABLE IV

The following compositions are in accordance with the invention.

	W	X	Y	Z	AA	BB	CC	DD	EE
<u>Spray-Dried Granules</u>									
LAS	10.0	10.0	16.0	5.0	5.0	10.0	-	-	-
TAS	-	1.0	-	-	-	-	-	-	-
MBAS	-	-	-	5.0	5.0	-	-	-	-
C ₄₅ AS	-	-	1.0	-	2.0	2.0	-	-	-
C ₄₅ AE ₃ S	-	-	-	1.0	-	-	-	-	-

[illegible]

HMC I							3.0		
<u>Dry-add particulate components</u>									
Any of Particle G to J	-	-	4.0	-	6.0	5.0	-	-	-
NACAOBS	3.0	-	-	1.5	-	-	-	5.5	-
NOBS/ LOBS/ DOBS	-	3.0	3.0	-	-	-	-	-	5.0
TAED	2.5	-	-	1.5	2.5	6.5	-	1.5	-
HMC II	-	-	-	0.7	-	-	1.0	3.5	0.5
QEA	-	-	-	0.2	0.5	-	-	-	-
Percarbonate	15.0	3.0	6.0	10.0	-	-	12.0	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.5	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate	-	-	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsuiated)	0.6	0.5	0.5	-	0.3	0.5	0.2	0.1	0.6
Suds suppressor	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
Citric acid	-	-	-	-	-	-	-	5.0	5.0
Dyed carbonate (blue, green)	0.5	0.5	?	2.0	-	0.5	0.5	0.5	1.0
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1	-	0.6	-
Dye	-	-	-	0.3	0.05	0.1	-	-	-
AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	-	-	-	0.8	-	0.5	0.8	0.5	1.0
Fillers up to 100%									

TABLE V

The following are high density and bleach-containing detergent formulations according to the present invention:

	FF	GG	HH
Agglomerates			
STPP/ Zeolite A	10.0	25.0	15.0
QAS	-	2.5	-
LAS	3.0	-	3.0
C45AS	3.0	2.0	4.0
QAS	-	-	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
HMC	2.0	-	1.5
CABP	0.8	1.0	0.5
Agglomerate			
NaSKS-6 (I) or (II)	15.0	-	-
LAS	8.0	-	-
AS	5.0	-	-
Spray On			
Perfume	0.3	0.3	0.3
C25E3	2.0	-	2.0
brightener	0.1	0.4	
photobleach	0.03	0.05	-
Dry additives			
QEA	1.0	2.0	-
Citric acid	5.0	-	2.0
Any of Particle G - J	-	7.0	
Carbonate	8.0	15.0	10.0

NAC OBS	6.0	-	5.0
HMC II	-	-	2.0
TAED		3.0	-
NOBS	-	2.0	-
Percarbonate	-	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
CMC	1.0	0.5	1.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

TABLE VI

5 The following liquid composition is in accord with the invention

Component	II	JJ	KK	LL
C ₁₂₋₁₅ alkyl ether (2.5) sulfate	38	38	38	38
C ₁₂ glucose amide	6.86	6.86	6.86	6.86
Citric Acid	4.75	4.75	4.75	4.75
C ₁₂₋₁₄ Fatty Acid	2.00	2.00	2.00	2.00
Enzymes	1.02	1.02	1.02	1.02
MEA	1.0	1.0	1.0	1.0

-40-

Propanediol	0.36	0.36	0.36	0.36
Borax	6.58	6.58	6.58	6.58
Dispersant	1.48	1.48	1.48	1.48
Na Toluene Sulfonate	6.25	6.25	6.25	6.25
QAS	1.0	1.0	-	1.0
QEA	2.0	2.0	2.0	-
CABP	-	-	1.0	0.5
HMC I or II	5.0-0.5	5.0-0.5	5.0-0.5	5.0-0.5
CMC or AC	1.0	1.0	2.0	-
Dye, Perfume, Brighteners,	<u>Balance</u>	<u>Balanc</u>	<u>Balanc</u>	<u>Balanc</u>
Preservatives, Suds Suppressor,		<u>e</u>	<u>e</u>	<u>e</u>
Other Minors, Water				
	100%	100%	100%	100%

TABLE VII

The following liquid detergent formulations are prepared according to the present invention

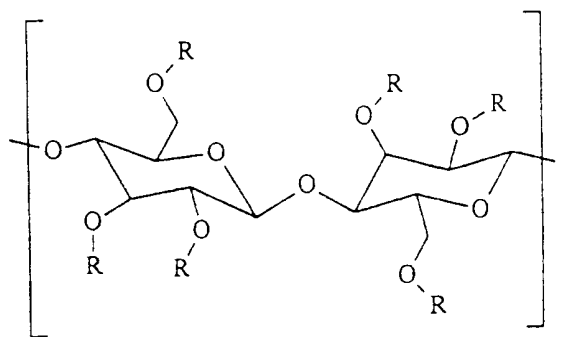
5

	MM	NN	OO	PP	QQ
LAS	11.5	9.0	-	4.0	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	16.0	-
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
STS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	3.0
Na hydroxide	6.0	2.0	3.5	4.0	3.0
Ethanol	2.0	1.0	4.0	4.0	3.0
1,2 Propanediol	3.0	2.0	8.0	8.0	5.0
Monoethanolamine	3.0	1.5	1.0	2.5	1.0
HMC I or II	5.0-0.5	5.0-0.5	5.0-0.5	5.0-0.5	5.0-0.5
CABP	0.5	0.5	-	-	-
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
CMC	0.2	-	0.5	-	1.0
DTPA	-	-	0.3	-	-

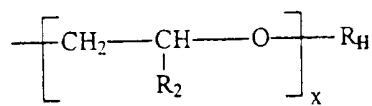
PVNO	-	-	0.3	-	0.2
Silicone antifoam	0.04	0.02	0.1	0.1	0.1

What is claimed is:

1. A detergent composition or component comprising a particulate hydrophobically modified cellulosic material, whereof at least 80%, preferably at least 90%, by weight has a particle size of below 1000 microns.
2. A detergent composition or component according to claim 1 whereby at least 80% or even 100% of the hydrophobically modified cellulosic material has a particle size of below 850 microns or even below 710 microns.
3. A detergent composition or component according to claim 1 or 2 whereby the hydrophobically modified cellulosic material comprises polymers of the formula



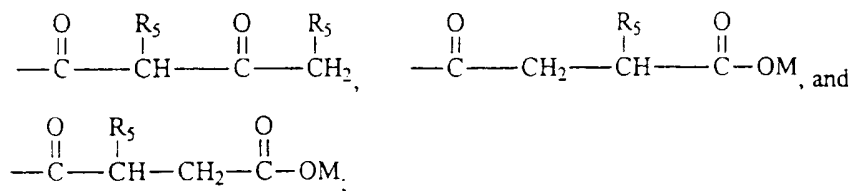
wherein each R is selected from the group consisting of R_2 , R_C , and



wherein:

- each R_2 is independently selected from the group consisting of H and C_1 - C_4 alkyl;
- each R_C is $\text{---}(\text{CH}_2)_y\text{---}\overset{\text{O}}{\parallel}\text{C---OZ}$,
wherein each Z is independently selected from the group consisting of M, R_2 , R_C , and R_H ;
- each R_H is independently selected from the group consisting of C_5 - C_{20} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{20} alkylaryl, C_7 - C_{20} arylalkyl, substituted alkyl, hydroxyalkyl,

C₁-C₂₀ alkoxy-2-hydroxyalkyl, C₇-C₂₀ alkylaryloxy-2-hydroxyalkyl, (R₄)₂N-alkyl, (R₄)₂N-2-hydroxyalkyl, (R₄)₃N-alkyl, (R₄)₃N-2-hydroxyalkyl, C₆-C₁₂ aryloxy-2-hydroxyalkyl,



- each R₄ is independently selected from the group consisting of H, C₁-C₂₀ alkyl, C₅-C₇ cycloalkyl, C₇-C₂₀ alkylaryl, C₇-C₂₀ arylalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl, morpholinoalkyl, cycloalkylaminoalkyl and hydroxyalkyl;
- each R₅ is independently selected from the group consisting of H, C₁-C₂₀ alkyl, C₅-C₇ cycloalkyl, C₇-C₂₀ alkylaryl, C₇-C₂₀ arylalkyl, substituted alkyl, hydroxyalkyl, (R₄)₂N-alkyl, and (R₄)₃N-alkyl;

wherein:

M is a suitable cation, preferably selected from the group consisting of Na, K, 1/2Ca, and 1/2Mg;

each x is from 0 to about 5;

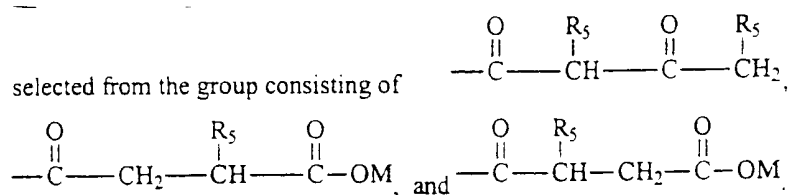
each y is from about 1 to about 5; and

provided that:

- the Degree of Substitution for group R_H is between about 0.001 and 0.1, more preferably between about 0.005 and 0.05, and most preferably between about 0.01 and 0.05;
- the Degree of Substitution for group R_C wherein Z is H or M is between about 0.2 and 2.0, more preferably between about 0.3 and 1.0, and most preferably between about 0.4 and 0.7;
- if any R_H bears a positive charge, it is balanced by a suitable anion; and
- two R₄'s on the same nitrogen can together form a ring structure selected from the group consisting of piperidine and morpholine.

4. A composition or component according to claim 3, wherein each R_H is independently selected from the group consisting of C_5 - C_{20} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{20} alkylaryl, C_7 - C_{20} arylalkyl, substituted alkyl, hydroxyalkyl, C_1 - C_{20} alkoxy-2-hydroxyalkyl, C_7 - C_{20} alkylaryloxy-2-hydroxyalkyl, $(R_4)_2$ N-alkyl, $(R_4)_2$ N-2-hydroxyalkyl, $(R_4)_3$ N-alkyl, $(R_4)_3$ N-2-hydroxyalkyl, and C_6 - C_{12} aryloxy-2-hydroxyalkyl.

5. A composition or component according to claim 3, wherein each R_H is independently



6. A detergent component or composition according to any preceding claim wherein the hydrophobically modified cellulosic material is present in a pre-formed particle comprising a carrier material and/ or a surfactant, and whereby preferably at least 80% of the material has a particle size of below 500 microns.
7. A detergent component or composition according to claim 6 wherein the preformed particle is an agglomerate, comprising one or more carrier materials selected from inorganic salts, silicates or aluminosilicates and an anionic and/ or nonionic surfactant.
8. A detergent component or composition according to claim 6, wherein the preformed particle is a spray dried blown powder particle, comprising one or more carrier materials selected from inorganic salts, silicates or aluminosilicates and an anionic and/ or nonionic surfactant.
9. A detergent component or composition according to any of claims 1 to 5 wherein the hydrophobically modified cellulosic material is in the form of a dry-add particle.

International Application No.
PCT/US 00/17532

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/22 C11D11/00 C11D11/02 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

C. DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category *	Citation of document, with indication, where appropriate, of the relevant passages	
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X	WO 98 28339 A (ALLIED COLLOIDS LTD) 2 July 1998 (1998-07-02) example 1 --- -/--	1,2

☒

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

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Date of the actual completion of the international search

3 October 2000

Date of mailing of the international search report

16/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Int. - National Application No
PCT/US 00/17532

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A	US 5 308 513 A (HARMALKER SUBHASH ET AL) 3 May 1994 (1994-05-03) claims 1,11	1
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P,A	DE 198 53 173 A (HENKEL KGAA) 25 May 2000 (2000-05-25) page 3, line 5 - line 45; claims 1,6,9-11	1

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International Application No

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